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The mobility of isolated polychlorinated biphenyl (PCB54) in 1,4-polybutadiene (PB) has been investigated by means of broadband dielectric spectroscopy. The aim was to provide new insights about the effect of the environment on the dynamics of PCB54. The authors' results indicate that PCB54 structural dynamics is neither independent of the PB matrix nor slaved to the matrix itself. The authors interpret these results as a consequence of the limited size of cooperatively rearranging regions (CRRs) involved in PCB54 structural relaxation possessing an effective concentration different from the macroscopic one. This implies a non-negligible influence of "self-concentration," already proven for the component segmental dynamics in polymer blends, also in the relaxation of binary mixtures involving low molecular weight glass formers. This allowed the evaluation of the size of CRR, which was about 1 nm for PCB54 in PB. This means that the cooperativity extends over the first shell around PCB54 molecules. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2740632]

I. INTRODUCTION

The dynamics of single component glass-forming liquids have been the subject of an overwhelming body of studies in the last decades. Interest in this field has been driven by the fundamental information that can be achieved on the still controversial problem of the glass transition. In recent years, an increasing number of works has been devoted to the investigation of the dynamics of multicomponent glass-forming systems. A common main signature of these systems is the heterogeneous nature of the dynamics, which manifests with a broadening of the response and, in many cases, the presence of two time scales related to the α relaxation, namely, the molecular motion associated with the glass transition. The latter phenomenon, often testified by the presence of two glass transition temperatures (T_g), has been observed in both experiments and simulations for a wide variety of systems such as polymer blends,[1–5] polymer-plasticizer systems,[6–18] and low molecular weight glass former binary mixtures.[19–22]

For polymer blends, the presence of two time scales, initially attributed to the role of thermodynamically induced concentration fluctuations,[23,24] has been recently explained, invoking the role of chain connectivity on the so-called "self-concentration."[25] This can be explained due to the limited size of the region involved in the dynamics related to the glass transition, namely, the characteristic length scale for structural relaxation which can be interpreted in terms of cooperatively rearranging regions (CRRs) proposed by Adam and Gibbs[26] and the presence of chain connectivity; i.e., the fact that in polymers two neighbors of one structural unit must also be units of the same polymer, the local concentration in the region involved in the dynamics is generally different from the macroscopic one and, in particular, richer in the component for which the dynamics are probed. While the possible role of concentration fluctuations in affecting the average relaxation time of the α process is still a matter of open debate,[27] experiments in dilute polymer blends have unambiguously demonstrated the crucial role of self-concentration for polyisoprene[28] (PI) and polystyrene[29] (PS) dynamics in different host matrices. In these systems, the dilute polymer is almost completely surrounded by the other polymer and concentration fluctuations are therefore minimized. Nevertheless the segmental dynamics of the dilute polymer are different from that of the matrix indicating that in the region involved in the α relaxation the effective concentration of the dilute polymer is larger than the macroscopic one.

Similar experiments have been performed to study the structural dynamics of diluted probe molecules, namely, tetracene and rubrene, in different host matrices.[30] Unlike dilute polymer blends, self-concentration effects were considered

to be negligible. Furthermore, Savin *et al.*[16] showed that several solvent-solvent systems display a temperature range for the glass transition as measured by differential scanning calorimetry almost as narrow as that of single component systems. This has led these authors to the conclusion that self-concentration must be a dominant parameter only for polymers due to the presence of chain connectivity that, even for dilute systems, imposes that at least two neighbors of the structural unit under investigation must be of the same polymer. This would mean that if self-concentration has a role in producing dynamic contrast in polymer blends as a consequence of just chain connectivity, the presence of two time scales for the α relaxation in molecular weight glass former binary mixtures reported in both experiments[19,22] and simulations[21] must be attributed to something else. However, it is noteworthy that experiments in dilute low molecular weight binary systems of 3-bromopentane (3BP) in 3-methylpentane (3MP) present a notable decoupling of the dynamics of the guest molecule from that of the host matrix.[20] Yet these results are not interpreted in terms of size of the region involved in the cooperative motion associated with the α process.

In this work, to get new insights on the effect of blending on the dynamics of low molecular weight glass formers, we probe the dynamics of dilute solutions of a polychlorinated biphenyl (PCB54) in 1,4-polybutadiene (PB) by means of broadband dielectric spectroscopy. The aim is to investigate to what extent the presence of the relatively fast PB affects the dynamics of PCB54. In particular, this would depend on the amount of PB participating in the cooperative rearrangement involved in the relaxation of PCB54. Our results clearly indicate that the dynamics of PCB54 is neither slaved to that of the host matrix nor equal to that of pure PCB54. In the framework of the theory of cooperative motion involved in the structural relaxation of glass formers, these results could be interpreted invoking the possible role of self-concentration for low molecular weight glass-forming systems in analogy to glass-forming polymers—chain connectivity being an additional ingredient for self-concentration for the latter systems. This interpretation allowed the determination of the size of CRR involved in the structural relaxation of PCB54 in PB. This was done in two ways: (i) through simple geometric considerations based on the dependence of PCB54 intermolecular distance on PCB54 concentration and (ii) incorporating the self-concentration concept into the Adam-Gibbs (AG) theory of the glass transition relating the relaxation time and the characteristic length scale of the α process to the configurational entropy.[26] Recently the latter approach has been successfully employed to describe the component segmental dynamics of miscible polymer blends and polymer-solvent systems.[31–34]

II. EXPERIMENT

The polychlorinated biphenyl was Monsanto's Aroclor 1254 (PCB54) with 54 wt % chlorine content, having a glass transition temperature $T_g=246$ K. The chlorine content corresponds to four to five chlorine atoms per PCB54 molecule, attached to the two condensed aromatic hydrocarbons that constitute the core of PCB54 molecules. This means that PCB54 is a rigid molecule. It was purchased from LGC Promochem and used as received. PB was purchased from Sigma-Aldrich. The molecular weight was $M_n=42\times10^4$ ($M_w/M_n=2$) and the glass transition temperature $T_g=178$ K. The microstructure of PB consisted of 36% *cis* and 55% *trans* units with the remaining 9% being 1,2-polybutadiene.

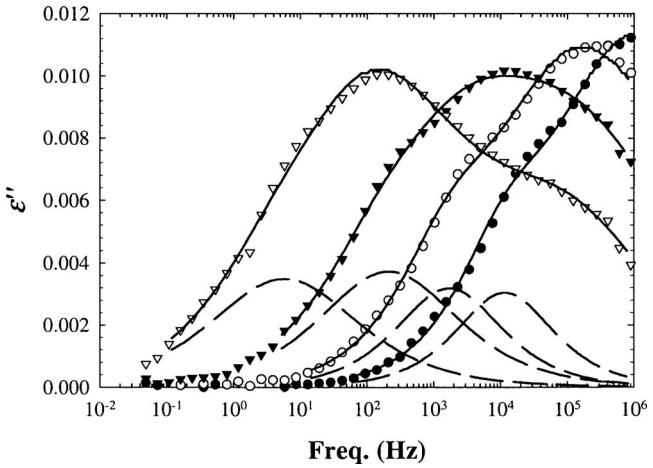

FIG. 1. Permittivity loss vs frequency for PCB54/PB mixture with 2 wt % PCB54 at the following temperatures: 223 K (filled circles), 213 K (open circles), 203 K (filled triangles), and 193 K (open triangles). Solid lines are the overall fits to experimental data through a sum of HN functions. Dashed lines are the contribution to the overall fits of PCB54 related dynamics. For clarity, the fitting curves related to the dynamics of PB α and β processes are not shown.

Homogeneous PCB54/PB mixtures were prepared by dissolving PCB54 and PB in toluene in the required proportions. The so-obtained solution was then poured on the bottom electrode of a dielectric cell. Golden-coated brass electrodes were used for all samples. Teflon spacers were also added to maintain a 0.1 mm constant thickness of the sample and to prevent the short circuit of the sample capacitor. Toluene was subsequently evaporated at room temperature for one day and in a vacuum until no weight loss was observed. No PCB54 weight loss was detected after this procedure, whereas toluene was fully removed. Mixtures with the following PCB54/PB weight ratios were prepared: 2/98, 5/95, 10/90, and 15/85.

Dielectric measurements were carried out on all PCB54/PB mixtures and on pure PB using a high precision dielectric analyzer (ALPHA, Novocontrol GmbH) and a Novocontrol Quatro cryosystem for temperature control with a precision of ±0.1 K. Measurements were performed over a wide frequency (10^{-2}–10^6 Hz) and temperature range in isothermal steps starting from the highest temperature.

III. RESULTS

Figure 1 displays the dielectric permittivity loss as a function of frequency at several selected temperatures for PCB54/PB system with 2 wt % PCB54. Two relaxational processes are visible in the available frequency window at all displayed temperatures and a third one appears at relatively high frequency at the lowest displayed temperature ($T=193$ K). In order to assign each relaxational process to a

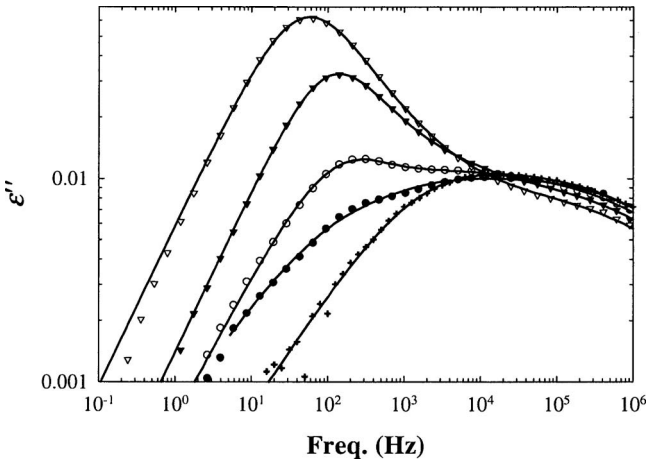

FIG. 2. Permittivity loss vs frequency at 203 K for pure PB (crosses) and PCB54/PB mixtures with the following weight percentages of PCB54: 2% (filled circles), 5% (open circles), 10% (filled triangles), and 15% (open triangles). Solid lines are the overall fits to experimental data through a sum of HN functions.

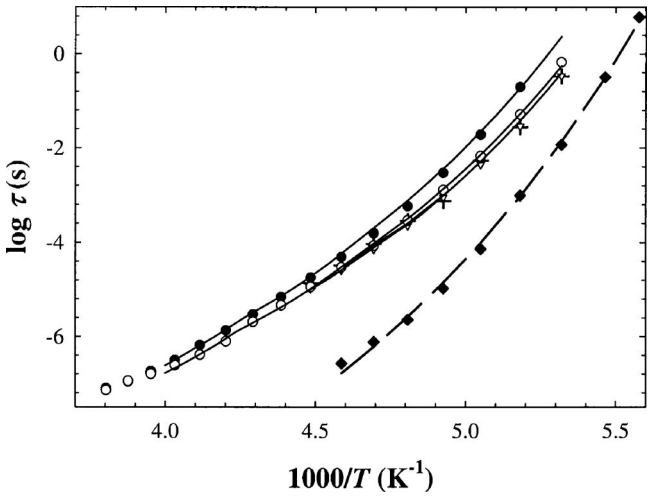

FIG. 3. Temperature dependence for the characteristic relaxation time related to the PCB54 dynamics in PB at the following weight percentages: 2% (crosses), 5% (open triangles), 10% (open circles), and 15% (filled circles). The temperature dependence of PB characteristic relaxation time is also shown (filled diamonds). The solid lines are the fits of the model incorporating the self-concentration concept in the AG theory to the mixture experimental data. The dashed line is the fitting of the AG equation to PB data.

specific molecular motion, it is worth comparing the permittivity loss versus frequency spectra for all PCB/PB mixtures together with pure PB dielectric response. This is done in Fig. 2 at $T=203$ K. By comparison with pure PB spectrum (crosses in Fig. 2), it can be concluded that the high frequency peak displayed at these temperatures by all PCB54/PB mixtures can be attributed to PB segmental relaxation. On the other hand, the low frequency peak, present only for systems containing PCB54 and increasing its strength with PCB54 content, can be assigned to the relaxation of the relatively less mobile PCB54 in PB. It is worthy of remark that, although a peak is not unambiguously discernable, the mixture with 2% PCB54 (filled circles in Fig. 2) presents a clear excess loss at relatively low frequency in comparison to pure PB (crosses in Fig. 2). This excess loss develops into a clear peak at higher PCB54 concentration even for the mixture with 5% PCB54 (empty circles in Fig. 2). Finally, the high frequency process present in the dielectric spectrum of PCB54/PB with 2 wt % PCB54 at 193 K can be unequivocally attributed to PB secondary relaxation.[35]

In order to extract the characteristic relaxation times of each process, the dielectric spectra were fitted by a sum of Havriliak-Negami (HN) functions that for the complex dielectric permittivity (ε^*) reads[36]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1+(i\omega\tau_{HN})^{\alpha_{HN}}]^{\gamma_{HN}}}, \tag{1}$$

where ε_∞ is the high frequency limit value of the dielectric constant, $\Delta\varepsilon$ is the dielectric strength of the relaxation process, and α_{HN} and γ_{HN} are the shape parameters of the HN function describing, respectively, the symmetric and asymmetric broadening of the complex dielectric permittivity. To reduce the number of fitting parameters, α_{HN} and γ_{HN} shape parameters for PB related relaxation in the mixtures were assumed equal to those of pure PB, the concentration of PB being always higher than (or equal to) 85 wt %. In addition, the relaxation strength was scaled to the relaxation strength of pure PB according to its concentration in the mixture. Finally, the relaxation time for PB related dynamics for the most diluted mixtures (2 and 5 wt %) was kept equal to that of pure PB. This means that for the most diluted mixtures the number of fitting parameters reduces to four, whereas for the others is never larger than five. A sum of HN functions accurately describes the dielectric spectra of all studied mixtures as shown in Figs. 1 and 2 by the solid lines. The dashed lines in Fig. 1 represent the contribution to the overall fitting of PCB54 related dynamics, which is relevant for this study. In the case of PCB54 related relaxation process and PB secondary relaxation, γ_{HN} shape parameter was always found equal to unity. In this case the HN function reduces to a Cole-Cole function.[37] The relaxation time corresponding to the permittivity loss maximum (τ_{max}), taken as representative of the mean relaxation time, was evaluated from τ_{HN} using the relation derived by Boersma *et al.*[38]

$$\tau_{max} = \tau_{HN}\left[\left(\sin\frac{\alpha_{HN}\pi}{2+2\gamma_{HN}}\right)^{1/\alpha_{HN}}\left(\sin\frac{\alpha_{HN}\gamma_{HN}\pi}{2+2\gamma_{HN}}\right)^{-1/\alpha_{HN}}\right]^{-1}. \tag{2}$$

Notice that for $\gamma_{HN}=1$, $\tau_{max}=\tau_{HN}$. The so-derived relaxation times are plotted in Fig. 3 as a function of the inverse temperature for PCB54 related relaxation process in all mixtures as well as for pure PB. The main feature arising from a first inspection of the figure is the relaxation process related to PCB54 whose characteristic time scale is in between that of pure PCB54 and PB. Notably PCB54 dynamics depend very weakly on its content in PB except for the mixture with 15 wt % PCB54, which decouples from the dynamics at lower concentrations displaying slightly slower relaxation times. A similar result was recently obtained by Huang *et al.*,[20] who found a concentration independent dynamics of 3BP in 3MP up to concentration of almost 10 wt % 3BP.

IV. CHARACTERISTIC LENGTH SCALE FOR STRUCTURAL RELAXATION

The results presented in the previous section have highlighted the following main issues: (i) the dynamics of dilute PCB54 decouples from that of the PB host matrix even for the lowest investigated concentration (2 wt % PCB54) and (ii) PCB54 related dynamics do not depend on the concentration of the mixture up to 10 wt % PCB54.

To interpret the first result, one has to consider to what extent the environment surrounding an isolated molecule affects its motion. In particular, in one extreme case the molecule under consideration can move independently of the dynamics of the surrounding environment. In this case, the relaxation time of the molecule will be that of the pure system. In the other extreme case, the molecular rearrangement can occur only if a large number of units surrounding the molecule under consideration move cooperatively. In this latter case, the dynamics of the molecule will be simply that of the host matrix if the relevant length scale is much larger than the molecular size. In the case of PCB54 dynamics in PB, none of the two extreme cases actually occurs, since the dynamics are intermediate between that of pure PCB54 and that of the PB host matrix. Therefore, from a qualitative point of view, this result can be interpreted assuming that the length scale involved in the PCB54 motion is neither small enough to make the dynamics equal to that of pure PCB54 nor large enough to be that of PB host matrix, i.e., not larger than several nanometers.

The localized nature of the dynamics invoked to explain the decoupling of PCB54 dynamics from that of PB also allows understanding the independence of PCB54 dynamics on its concentration in the mixtures containing up to 10 wt % of PCB54. In particular, if the distance between two PCB54 molecules is on average larger than the cooperative length scale, only one PCB54 molecule will participate in the rearrangement associated with the α process, the rest being PB basic structural units. Only when the concentration of PCB54 will be large enough to bring two PCB54 molecules close enough that one of the two enters the CRR of the other, the dynamics will start suffering a slowing down. In other words, there will be a threshold PCB54 concentration above which the CRR will be composed of more than one PCB54 particle. For clarity, in Figs. 4(a)–4(c) we schematically draw the scenario where the distance between two particles is larger than the size of CRR, where one molecule is just about to interfere with the dynamics of another molecule of the same type and where other molecules participate in the cooperative rearrangement of another of the same type. According to this interpretation and to our results this threshold concentration should be between 10 and 15 wt % PCB54. This allows through simple geometric considerations the indirect estimation of the size of CRR. The average distance between the centers of two nearest neighbor molecules [a in Fig. 4] can be written as a function of the macroscopic weight fraction ϕ

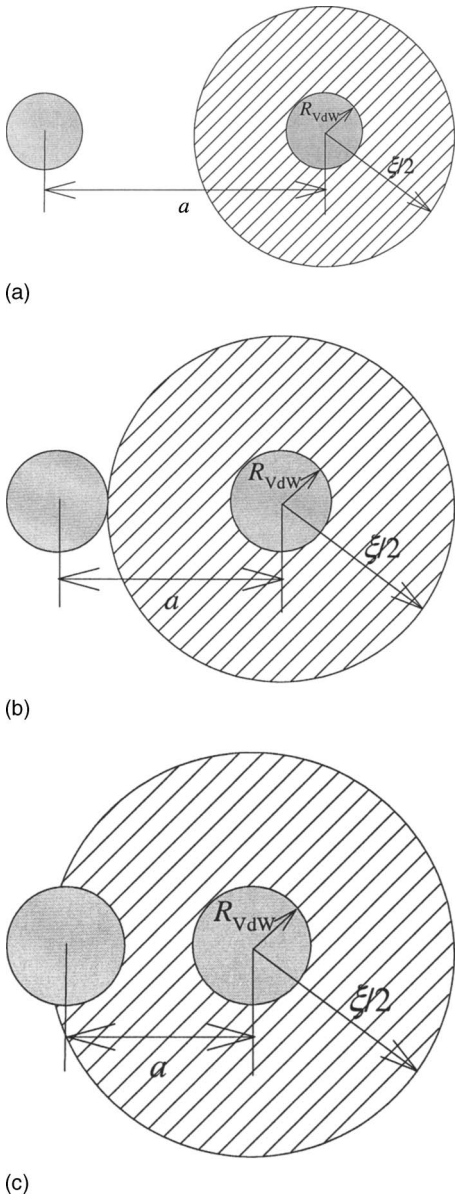

FIG. 4. Schematic illustration of two molecules of the same type immersed in a medium in relation with the size of CRR: (a) the two molecules are far from each other and do not interfere with each other CRR; (b) one molecule is just about to enter the CRR of the other; and (c) one molecule is within the size of CRR and, thereby, enters the CRR of the other.

$$a = \left(\frac{4}{3}\frac{\rho_{PCB54}}{\rho_{PB}}\frac{\pi}{\phi}\right)^{1/3} R_{vdW}, \tag{3}$$

where R_{vdW} is PCB54 van der Waals radius, ϕ is PCB54 macroscopic weight fraction, and ρ_{PCB54} and ρ_{PB} are the density of, respectively, PCB54 and PB. For PCB54, R_{vdW} = 3.67 Å as calculated using the approximation of Zhao *et al.*[39] The PCB54 and PB densities are ρ_{PCB54} = 1.51 g/cm^3 and ρ_{PB} = 0.97 g/cm^3. The use of Eq. (3) allows determining the distance between centers for the mixture with 10 and 15 wt % PCB54, namely, the two compositions between which a change in PCB54 dynamics occurs [scenario of Fig. 4(b)]. This is a = 1.27 nm and a = 1.11 nm, respectively, for the mixtures with 10 and 15 wt % of PCB54. Since at the threshold concentration $\xi = 2(a - R_{vdW})$, where ξ is the diameter of CRR [see Fig. 4(b)], it is possible to conclude that the

size of CRR ξ for the dynamics of isolated PCB54 molecules in PB must be comprised between 1.4 and 1.9 nm. It is noteworthy that the previous treatment was developed considering a homogeneous distribution of PCB54 molecules in PB, namely, a single intermolecular distance between PCB54 particles. However, a distribution of distances should be expected instead. This means that the estimated value for the size of CRR must be considered as an upper bound of the actual one, since the distance between the closest PCB54 molecules at the concentration threshold will be smaller than the average.

V. SIZE OF CRR FROM ADAM-GIBBS THEORY AND SELF-CONCENTRATION

In the former section of the paper, the decoupling of PCB54 dynamics from that of PB was interpreted according to the localized nature of the α relaxation in glass-forming systems. As anticipated in the Introduction, this interpretation can be rationalized invoking the concept of "self-concentration" giving rise to an effective concentration in the volume relevant for structural relaxation larger than the macroscopic one.

A complementary estimation of the size of CRR can be performed analyzing the above experimental results though a model, recently proposed by us,[31,34] that incorporates the self-concentration concept with the AG theory of the glass transition. The model has been already successfully employed to describe the component dynamics of miscible polymer blends[31,32,34] and that of polymers in concentrated solutions.[33,34] In what follows, we adapt the model to describe the dynamics of low molecular weight glass formers, such as PCB54, in mixtures. More details about the model can be found in Refs. 31 and 34. The application of the AG model in mixtures relies on the evaluation of the configurational entropy and of the parameter C of the AG equation[26] as a function of the effective concentration to calculate the component relaxation time as

$$\tau = \tau_0(\phi_{\text{eff}})\exp\frac{C(\phi_{\text{eff}})}{TS_c(\phi_{\text{eff}})}, \tag{4}$$

where S_c, C, and τ_0 are, respectively, the configurational entropy, a temperature independent parameter, and the preexponential factor. All these quantities must be calculated in the volume relevant for the structural relaxation, i.e., in the microscopic volume where an effective concentration larger than the macroscopic one must exist due to self-concentration effects. The effective concentration, i.e., the concentration experienced by the relevant volume for segmental relaxation, is related to the self-concentration by

$$\phi_{\text{eff}} = \phi_s + (1-\phi_s)\phi, \tag{5}$$

where ϕ_{eff}, ϕ_s, and ϕ are, respectively, the effective, the self- and the macroscopic concentrations. In the case of low molecular weight glass formers, the self-concentration ϕ_s is defined as the volume fraction occupied by a molecule within a sphere of radius R_c centered around the same molecule. The parameters of the AG equation can be calculated assuming a linear combination of the properties of the pure components through the effective concentration in the CRR (for the preexponential factor the linear combination is employed for the logarithm).[34]

The linear combination of the configurational entropies of the pure components implies that the interaction parameter between PCB54 and PB is negligible,[34] whereas is an empirical assumption for the parameter C and the preexponential factor. However, it is noteworthy that these two parameters only rarely are very different in a large variety of glass formers. Regarding the specific interactions between PCB54 and PB, which might lead to strong deviation from ideal behavior, it is worth noting that our mixtures are always in the dilute regime, where strong deviations from ideality can be ruled out. In addition, PCB54 and PB mostly interact through van der Waals forces and specific preferential interactions, as in hydrogen bonded liquids, can be excluded. Due to the experimental inaccessibility of the configurational entropy, we have exploited the proportionality of this quantity with the excess entropy, namely, the entropy of the liquid in excess to that of the corresponding crystal. The configurational entropy for PB was extracted employing the approach of Di Marzio and Dowell[40] and accounts for 91% of the total excess entropy.[41] Regarding the configurational fraction of the excess entropy of PCB54, no data are available in the literature. Nevertheless these data have been obtained for several low molecular glass formers possessing a chemical structure comparable to that of PCB54 such as toluene and *ortho*-terphenyl.[42] We have therefore fixed the configurational fraction of the excess entropy of PCB54 to 70%. A linear form of the excess specific heat, $\Delta C_p = C_P^{\text{melt}} - C_P^{\text{crystal}} = a + bT$, where a and b are material specific constants, was employed to obtain the excess entropy.[43] Calorimetric data in the liquid and glassy state were taken from the literature from both PB (Ref. 44) and PCB54.[45] The excess entropy of the pure components was obtained by integrating the relation $\int_{T_K}^{T}[\Delta c_p(T)/T]dT$, where T_K is the Kauzmann temperature, namely, the temperature where the entropy of the liquid equals that of the crystal. Due to the lack of crystalline specific heat data for glass-forming polymers, the latter quantity was determined by identifying it with the temperature where the relaxation time of the α process tends to diverge.[46–48] Hence, the knowledge of the parameters a and b allows the fitting of pure PB and PCB54 dynamics data through the AG equation (dashed lines in Fig. 3) to obtain C, τ_0, and T_K. Dynamics data for PCB54 are taken from Ref. 49. These parameters are listed in Table I together with the calorimetric parameters a and b and T_g.

An important ingredient for the application of the model is the connection between the size of CRR (ξ) and the configurational entropy,[26,31,34]

$$\xi/2 = R_c(\phi_{\text{eff}}) = \alpha[S_c(\phi_{\text{eff}})]^{-1/3}, \tag{6}$$

where R_c is the equivalent radius of CRR and α is a material specific parameter that can be evaluated from the fitting of dynamics data. For low molecular weight glass formers, R_c (or ξ) can be related to the self-concentration, and therefore the effective concentration, through simple geometric considerations,

TABLE I. Relevant parameters for PCB54 and PB components of all mixtures. Data for the C parameter of the AG relation and for the parameters a and b of the specific heat are referred to a per mole of monomer basis for PB and to a per mole of PCB54 basis for PCB54.

	T_g (K)	T_K (K)	C (kJ/mol K)	log τ_0 (s)	a (J/mol K)	b (J/mol K^2)
PCB54	246	167	153	−20	118.9	−0.23
PB	178	129	29	−15.5	42.8	−0.08

$$R_c = R_{\mathrm{vdW}} f_s^{-1/3}. \quad (7)$$

The combination of Eqs. (4)–(7) can be solved as a function of the effective concentration (self-concentration) for each value of α. The selected value of α is that providing an effective concentration that, once introduced in Eq. (4), is able to best reproduce the experimental relaxation times. The solid lines in Fig. 3 are the best fitting of the model to experimental data. As is possible to observe, the result of the fitting is satisfactory. However, it is worth noting that a single value of α could not provide a good fitting of all the data and, therefore, α was allowed to vary with the concentration. This could in principle be due to the different contributions of each component in the CRR to the overall value of α, this being material specific.[31,34] In particular, in a recent paper we have shown that a mixing rule of the intrinsic values of the α parameter of PI and polyvinylethylene (PVE) through the effective concentration allows the prediction of the characteristic time scale of the component dynamics of the two polymers in PI/PVE blends.[34] To further clarify this point, in Fig. 5 we plot the value of α used to fit data as a function of the effective concentration. From the inspection of the figure, an approximate linear correlation can be detected. Furthermore, extrapolation to 100% PB leads to an intrinsic value of α for PB equal to $\alpha = 25$ Å J$^{1/3}$ mol$_{\mathrm{PCB54}}^{-1/3}$ K$^{-1/3}$. This value rewritten on a per mole of butadiene basis reads $\alpha = 14.6$ Å J$^{1/3}$ mol$_{\mathrm{PB}}^{-1/3}$ K$^{-1/3}$, and can be compared to that already obtained for other polymers with similar structure, such as PI that possesses a value of $\alpha = 17.5$ Å J$^{1/3}$ mol$_{\mathrm{PI}}^{-1/3}$ K$^{-1/3}$. The similarity between the two values is a good indication of the reliability of the extrapolation of the value of the α parameter to 100% PB.

The achievement of the effective concentration necessary to fit dynamics data allows the determination of the characteristic length for the dynamics of PCB54 in PB through Eq. (7) that relates the size of CRR to the self-concentration via the van der Waals radius. To extract the self-concentration from the effective concentration, we note that the two quantities simply coincide in the dilute regime when PCB54 molecules are surrounded exclusively by PB molecules. As commented in the previous section of the paper, this is true up to a concentration of 10 wt % PCB54. On the other hand, the self-concentration can be calculated through the equation $\phi_s = (\phi_{\mathrm{eff}} - \phi)/(1-\phi)$ for the mixture with 15 wt % PCB54. The so-obtained size of CRR is plotted in Fig. 6 (left axis). As can be observed, an increasing length scale with decreasing temperature is obtained, comprised between 1 and 1.2 nm depending on the temperature. The mixture with the largest concentration of PCB54 displays a tendency to a larger size of CRR compared to the other mixtures. In Fig. 7, the temperature dependence of the self-concentration is displayed for all mixtures. Values between 0.1 and 0.7 depending on the temperature and the mixture have been obtained. At temperature close to T_g, values around 0.1–0.2 have been found for the self-concentration, which are smaller than for polymers,[25,27–34] but of the same order of magnitude of the low molecular weight glass former rubrene in various environments.[30] From the observation of Fig. 7, a rather strong temperature dependence of the self-concentration is also evident. Similar results have been found for the component dynamics in polymer blends[27,31–34] and polymer-solvent[33,34] mixtures. This implies that the mean-

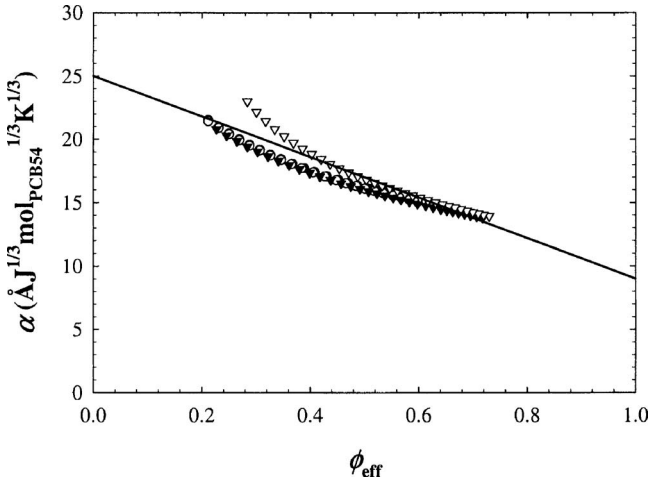

FIG. 5. Effective concentration dependence of the constant relating the size of CRR to the configurational entropy for the mixture with the following weight percentage of PCB54: 2% (filled circles), 5% (empty circles), 10% (filled triangles), and 15% (empty triangles). The straight line is the average linear fitting to experimental data.

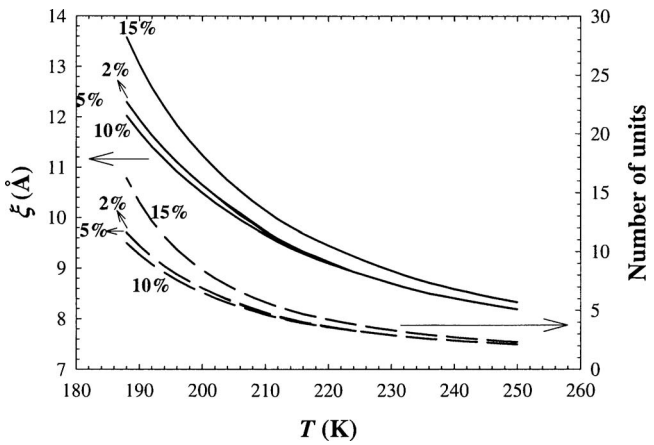

FIG. 6. Temperature dependence of the diameter of CRR (left axis) and the number of basic structural units participating to the cooperative rearrangement (right axis) for all PCB54/PB mixtures.

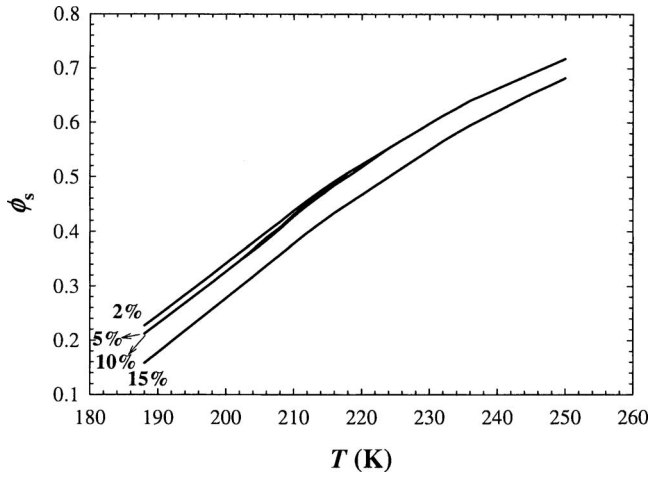

FIG. 7. Temperature dependence of self-concentration for all PCB54/PB mixtures.

field approach by Lodge and McLeish,[35] based on a temperature independent self-concentration, is at least questionable.

VI. DISCUSSION

In the previous sections of the paper, we have interpreted the decoupling of PCB54 dynamics in PB as a consequence of the limited size of the CRR inducing an effective concentration different from the macroscopic one. Starting from this interpretation we have attempted to determine the size of the CRR using two different approaches: (i) one based on the onset of the undiluted regime leading to a shift in the dynamics at a particular threshold concentration and (ii) another one where a model incorporating the concept of self-concentration in the AG theory was employed. The former approach, which was based on a homogeneous distribution of the PCB54 molecules in PB, resulted in a size of CRR of about 1.5 nm, whereas for the latter approach this size was between 1 and 1.2 nm. Considering that, as previously commented, the former approach overestimates the size of CRR, the agreement between the two approaches is excellent and, therefore, the estimation of the size of CRR can be considered highly reliable.

Starting from the obtained size of CRR, the number of structural units involved in the cooperative rearrangement can be evaluated. This can be done from the knowledge of the volume of the basic structural unit of PCB54 and PB. For the former species the basic structural unit is simply the whole molecule, as PCB54 molecule lacks internal degrees of freedom. For PB the basic structural unit can be identified with the monomer, since a crankshaft motion is allowed around the 1,4 axis. Therefore, the volumes of the basic structural unit of PCB54 and PB are, respectively, $V_{\mathrm{PCB54}}=206$ Å^3 and $V_{\mathrm{PB}}=72.5$ Å^3. Considering that for PCB54 dynamics in PB each CRR would be composed of one PCB54 surrounded by PB molecules, from the size of CRR and the volumes of each basic structural unit one can calculate the number of particles taking part in the cooperative rearrangement. This is strictly true for mixtures with up to 10 wt % PCB54, whereas, as previously observed, for the mixture with 15 wt % PCB54 more than one PCB54 molecule can enter the CRR. The number of basic structural units taking part in the cooperative rearrangement is shown in Fig. 6 (right axis) as a function of temperature for all investigated mixtures. As can be observed, for the mixtures with up to 10 wt % PCB54 the number of units entering the CRR varies from about 2 to more than 10 when the temperature is lowered from T_g+60 to T_g. This means that the mild temperature dependence of the radius of the CRR results in a rather strong dependence of the number of units participating in the structural relaxation. It is interesting to note that the mixture with 15 wt % PCB54, where according to our interpretation more than one PCB54 molecule participates in the CRR, displays larger sizes of CRR. This result can imply that PCB54 requires a larger volume involved in the cooperative rearrangement. Experimental data on more concentrated solutions of PCB54 in PB are needed to clarify this point. However, this hypothesis seems to be in agreement with the estimation of Rizos and Ngai,[50] who—studying PCB54 dynamics in PI and PB with various molecular weights—speculated that the size of CRR of PCB54 should be around 3 nm at T_g.

The involvement of about ten structural units in the cooperative rearrangement of PCB54 in dilute mixtures with PB at the T_g implies that CRRs are mainly composed of PB units. Starting from this observation, one can rationalize the relatively low sizes of CRR found for dilute mixtures. These can be compared with the length scales found for polymers with similar flexibility. Among them, poly(vinyl methyl ether) is the one displaying the most similar length scale, namely, around 1 nm.[31,52] Other polyolefins for which the size of CRR has been estimated, such as PVE and PI,[34] present the size of CRR of the order of 1.5 nm, i.e., slightly larger than that of PB. In the case of PI and PVE the presence of a side group might be responsible for the larger cooperative sizes. The relatively small characteristic length scale found for an ensemble mostly composed of PB can be explained considering the high flexibility of this polymer that results in a relatively short interchain distance. This was very recently reported by Narros *et al.*[51] by means of neutron diffraction with polarization analysis and molecular dynamics simulations. They found that the first peak of the static structure factor, corresponding to the intermolecular correlation, was located at about 1.4 Å^{-1} that corresponds to an intermolecular distance of about 4.5 Å. This value, together with the size of CRR found for dilute mixture of PCB54 in PB, implies that only the first shell around each PCB54 molecule is involved in the molecular rearrangement. This result is in agreement with a very recent analysis on the size of CRR of several glass-forming polymers, for which a similar correlation between the size of CRR and the intermolecular distance was found.[52]

The interpretation of the decoupling of PCB54 dynamics from that of PB in dilute mixtures of the first compound in terms of cooperative length scale involved in the structural relaxation could also explain the decoupling of 3BP dynamics from that of 3MP recently observed by Huang *et al.*[20] Apart from this decoupling, in analogy with our results, they also found that 3BP dynamics displays a slight dependence, if any, on its concentration in the mixture up to a concentra-

tion of about 10 mol % of 3BP. Steeper concentration dependence appears at higher concentrations in agreement with the hypothesis of a threshold concentration above which other 3PB particles enter the CRR of one 3PB molecule. This implies a cooperative length scale of the order of 1 nm also for 3BP dynamics in 3MP.

Finally, it is also worth discussing the conclusion recently achieved by Ediger *et al.*[30] that self-concentration plays a minor role for low-molecular weight glass formers. A first inspection of the probe molecules $T_g(s)$ shift with respect to that of the matrix certainly indicates that self-concentration effects are more important for PI, i.e., a polymeric glass former, than for the low molecular weight glass formers tetracene and rubrene. However, a closer inspection to the $T_g(s)$ shift of the two probe molecules with respect to that of the host matrix suggests that also in this case an effect of the local environment to the T_g of the probe molecule exists, though smaller than for glass-forming polymers. This indicates that self-concentration also plays a role in affecting the dynamics of low molecular weight glass formers, although the absence of chain connectivity implies a less notable effect. In other words, chain connectivity is only one ingredient inducing a local environment richer in one component in mixture, another important factor being the localized nature of the glass transition.

VII. CONCLUSIONS

We have investigated the dynamics of dilute PCB54 in PB to get insights about the influence of the environment on the mobility of low molecular weight glass formers. We found that the dynamics of isolated PCB54 molecules is neither slaved to that of PB nor that of pure PCB54. This result has been attributed to the limited size of the volume involved in the relaxation, namely, the CRR of the AG theory. This interpretation is in agreement with the concentration independence of the relaxation time related to PCB54 dynamics up to a threshold concentration, which marks the involvement of more than one PCB54 in the CRR. The characteristic length scale for structural relaxation has been determined in such a way and compared to that extracted from the application of a model combining the AG theory with the self-concentration concept. The sizes of CRR obtained with the two approaches were in good agreement and of the order of 1 nm. This length scale implies the involvement of the first neighbors in the cooperative rearrangement at T_g, a feature that might be a general issue in glass-forming liquids.

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